Beyond GTL-FT: The Oxygenate Option - Methanol and DME

Dr. Theo H Fleisch, Distinguished Advisor, BP America
Dr. Ronald A. Sills, Gas Conversion Network Leader, BP America
BP E&P Technology, P.O. Box 3092, Houston, TX, 77253, U.S.A.

ABSTRACT
The monetization of the world’s large, remote gas reserves is the main driver for the advancement of Gas-to-Liquid (GTL) technologies where GTL has become synonymous for Fischer Tropsch (FT) technologies. Looking to other gas-derived liquids beyond GTL-FT, the conversion of natural gas into oxygenates is a chemical business today which is poised to transition into new high-volume fuel and chemical markets.

The focus of this paper is the ever-increasing global activities to commercialize methanol and DME for large-scale markets such as fuels for power generation and chemical feedstock for ethylene and propylene production; DME for domestic home cooking/heating; and DME as a diesel alternative. Price competitiveness with conventional fuel will also be discussed.

This emerging oxygenates business is being driven by the:
(a) Building of larger plants with low-cost gas producing methanol which is competitive with conventional hydrocarbon fuels and feedstocks. In mid-2004, BP and Methanex started production from the Atlas plant in Trinidad. This plant is the industry pacesetter since it is the world’s largest methanol plant. With a capacity of 5,000tpd, it is twice the size of previous world-scale plants. Nearly all new plant announcements are now equal to or exceeding this size, with plant proposals up to 15,000tpd which is equivalent to a 50,000bpd GTL plant monetizing about 500 MMscfd of gas.
(b) Development of new markets for DME - a new environmental-friendly fuel with multiple new large-volume fuels markets. DME can be economically co-produced with methanol. Organizations leading this effort are the International DME Association, Japan DME Forum and the Korea DME Forum.

This paper shows that the great potential of oxygenates, as clean fuels and chemical feedstocks for the 21st century, is beginning to be realized. Methanol is the enabling product in a “Natural Gas Park”. Significant global collaboration efforts are providing a foundation for creating a new oxygenate business.

1. Background and Context
The main drivers for this emerging oxygenates business are:
  o Monetization of remote gas or gas that today does not have a market.
  o Ability to make gas-derived:
    o Clean synthetic fuels substitutes/alternatives for LPG, diesel, and gasoline. These synthetic fuels could use existing infrastructure with only minor modifications, except for the diesel alternative, DME.
    o Olefins via the methanol to olefins (MTO) or Methanol to Propylene (MTP) technology.
  o Readily-available production technology for making methanol and DME.
  o Multiple feedstocks, in addition to natural gas, such as coal and biomass.
  o Multiple-markets:
    o Being developed and tested - methanol and DME for power generation, domestic home cooking/heating, transportation, as a hydrogen carrier and as an economical chemical intermediate,
    o Market applications testing in Asia, particularly Japan, China, Korea and Iran.
  o Economic viability due to large-size plants with low-cost gas using conventional technology.

2. Methanol Industry
Methanol is an important chemical business today with a global demand of about 32 million tpy. Global demand is expected to grow modestly to 35 million tpy by 2008 because of phase-outs of MTBE, predominantly in North America. Despite this slow increase in demand, numerous very large plants are being built, with about 15 million tpy of new capacity coming online between 2004 and 2008. Most importantly, a step change has occurred away from the traditional 2,500 tpd world-scale plants to much larger plant sizes.

The world’s largest methanol plant, the Atlas Methanol plant, which is twice the size of previous world scale plants at 5,000 tpd or about 1.7 MMtpy capacity, started up in mid-2004. Jointly owned by Methanex and BP, the plant is located in
Trinidad. This plant has set a new benchmark with numerous followers advocating even larger plants. Another doubling of capacity to more than 10,000 tpd (3.4 MMtpy) is anticipated within 5-10 years. All announced new large plants have been or are being built at locations with low-cost gas allowing lower production costs.

This trend of rapidly increasing plant sizes with access to low cost feedstock leads to rationalization of higher cost producers but also enables and requires the development of new, large markets. In the past few decades, the average delivered price of methanol was about $150/ton, which corresponds to about $7/MMBTU. With fuel prices typically between $4 to 5/MMBTU (@ $20/bbl crude oil), methanol could not compete in the fuel market. However, economy of scale and low-cost feedstocks are driving the delivered methanol cost to about $100/ton, which is competitive in the fuel market. The PetroWorld projects in Qatar and West Africa with up to 15,000 tpd capacity target the power generation market with crude methanol. From a market perspective, great strides have been made in the understanding of methanol as a turbine fuel for power generation. Commercial guarantees are now available from major turbine manufacturers for methanol and DME. Both exhibit record efficiencies and very low emissions [2].

Another potentially very large, new market for methanol could be MTO (methanol-to-olefins) technology. Again, the technology originally developed by Mobil, but never commercialized), with modified approaches by UOP/NorskHydro [3] and Lurgi’s MTP (methanol to propylene) technology [4] basically awaits low-cost methanol/DME to be commercially viable. The project led by Eurochem in Nigeria aims at the production of polypropylene and polyethylene from Methanol/DME using the UOP/NorskHydro technology at the 7,500 tpd plant size. This plant size constitutes about 8% of the world methanol market but provides only enough feedstock for one world scale ethylene/propylene plant. Thus, both power generation and MTO can transition methanol to a large combined fuel and chemical business.

3. DME

Methanol has long been considered the centerpiece of a “Gas Refinery” or “Natural Gas Park” with a multitude of derivatives. DME, currently one of the low-volume derivatives, could emerge as the highest volume product because of its multi-purpose applications.

DME can be made by converting methanol, either as finished product or as crude methanol, by the dehydration reaction in a fixed-bed reactor, followed by distillation.

\[
2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}
\]

Catalyst
300˚C - 400˚C
150 - 300 PSIG

This process is relatively simple and has been practiced for many years to make DME for the small aerosol propellant market as well as on a large scale in the New Zealand Gas to Gasoline plant using Mobil Methanol-to-Gasoline (MTG) technology from 1985 to the early 1990's. (DME is an intermediate chemical in the MTG process.)

The potential of DME is best understood when one recognizes that DME is basically a synthetic LPG. DME has a lower heat content although with some additional attractive features such as high cetane compression ignition combustibility and easy reformability into hydrogen. Since the work by Amoco (now BP) and Haldor Topsoe in the early nineties [1, 5, 6, 7], DME has become the subject of numerous studies. Over the last several years, a global recognition of the potential of this multi-purpose fuel and chemical feedstock can be seen manifested by numerous events such as the formation of the International DME Association (IDA) in 2001 to promote public awareness and use of DME and the formation of the Japan DME Forum (JDF). The JDF coordinates multiple programs which are part of a large Japanese National DME Initiative, costing over $200 million in 2002-2005, to develop and commercialize DME manufacturing technology, shipping/distribution and marketing for multiple end-use applications such as diesel alternative, synthetic LPG and power generation. Japan is clearly a leading player in the global DME effort at this time. The IDA initiated a website, www.aboutdme.org, to serve as a global DME information center. More recently, in 2002, the Korea DME Forum (KDF) was formed to advance the understanding and use of DME in Korea. These three organizations represent about 160 companies, technical institutes, universities and individuals.

Some technology providers offer closely integrated Methanol/DME plants. The DME Development Co., Ltd is demonstrating a slurry DME process at a large 100 ton/d scale [8, 9, 13], which could be ready for commercialization by 2006. DME can be made from many feedstocks, including biomass with exciting efforts in Sweden (bio-DME) and coal in China, using available gasification technologies.
Recent DME developments include:

- **LPG Alternative for Domestic Use**: A theoretical study conducted by BP and Arthur D. Little [10] showed that blends leading to gas-phase concentrations up to 10% DME in LPG are likely to be acceptable for residential and commercial applications, with no adjustments to combustion equipment. Higher DME blends will likely be acceptable with some adjustments. This study used Weaver Indices, which represent major combustion phenomena. An experimental study by Snamprogetti and ENI [11] concluded that mixtures of 15-20% DME in LPG was feasible without modification to infrastructure.

- **Vehicle and Engine Studies**: Numerous vehicle/engine research and development and demonstrations activities are being conducted and have been reported at the First International DME Conference (DME1) and IDA Meetings in 2002 [12] by McCandless and Boehman in the U.S.A.; Landalv and Sorenson in Europe; Goto, Kajitani, Oguma and Sato in Japan; Daeyup Lee in Korea; and Cipolat in South Africa.

- **Production Technology Developments and Plant Designs and Economics** have been reported by JFE Holdings, Lurgi, Haldor Topsoe and Toyo [12, 13]. Developments to use biomass as feedstock in Sweden are progressing [12, 13].

DME can be economic today but further cost reductions are important. Numerous studies have shown that at scales above 5,000 tpd DME and 7,500 tpd methanol commercially attractive projects may be achievable.

A very comprehensive collection of health, environmental and safety data by DuPont shows that DME is safe for use can be found at: [http://www.epa.gov/chemrtk/dimethr/c12794tc.htm](http://www.epa.gov/chemrtk/dimethr/c12794tc.htm).

### 3.1. Opportunities: Major Market Developments

The potential markets for DME are very large. The large (>200MMtpy) and rapidly growing LPG market can absorb large volumes of DME. A market study presented by JFE Holdings (Japan), the total potential market in Asia, including Japan, China, India, South Korea and Taiwan is about 200 million TPY in 2020. This market consists of 73 million TPY for transport, 70 million TPY for electricity generation and 50 million TPY for residential use.

The on-going major market developments include:

- **China**:
  - First DME for fuels plant, producing 10,000 TPY from methanol, was built in mid-2003 by Toyo Engineering for the Lutianhua Group in the Sichuan Province. The DME is being blended with LPG and used for domestic cooking. Since the market acceptance was successful, the Lutianhua Group contracted with Toyo Engineering to build a 110,000 TPY plant to be completed in 2005.
  - In the Shandong Province, Shandong Jiutai Chemical Industry started up a 30,000 TPY DME from coal-derived methanol plant in December 2003. Construction on a 60,000 TPY plant started in January 2004. They plan to increase capacity to 1 million TPY by 2009.
  - The potential residential market in China is 23 million TPY (2020), according to the market study presented by JFE Holdings.

- **Iran**:
  - The National Petrochemical Company of Iran is planning to build a 800,000 TPY fuel- and propellant-grade DME from methanol, produced in a new plant using Lurgi technology, in Banda Assaluyeh, Iran, using methanol dehydration technology from Haldor Topsoe A/S of Denmark. The plant is expected to start up in 2006. The major market is to blend with LPG for domestic consumption - freeing LPG for export. Iranian market studies show that about 400,000 TPY DME could be marketed as a 20 wt% mixture with LPG. Iran plans to have 3.4 million TPY methanol capacity by 2007.

- **Other Countries** (More details to be provided in the presentation.): 
  - In Japan, the Japan DME Forum is coordinating multiple programs, costing about $200 million over 2002-2005, on DME utilization, production, ocean transportation and codes & standards.
  - Significant activities in Korea, Sweden, Russia, Italy, U.S.A. and Brazil.

### 3.2. Challenges

The emerging DME business faces numerous challenges. Commercial challenges include
resistance to new alternative fuels, new infrastructure costs, need for new partnerships in the value chain, high investment costs (financing) for large integrated projects, competition with LNG and GTL projects and customer acceptance of new fuels.

Among the technical challenges are the large sizes of the DME manufacturing plants though the technologies are proven. LPG Tanker modifications/optimizations are a minor challenge. Infrastructure challenges only need to be overcome in diesel transportation application while they are small or non-existent in LPG and power market applications.

Global challenges include the development of international standards and just raising the overall awareness of these new GTP opportunities. The oxygenates have to compete with the better known GTL-FT, hydrogen fuel cells and LNG technologies and businesses for attention and funding. New global collaborations need to be formed. The lack of a first successful large-scale plant and market is another drawback that will be, however, overcome soon.

3.3. Economics

The estimated CIF price of DME (at 15% IRR) in Japan is [13]:
- From the Middle East, varies from $3.7-$4.8/MMBtu with gas at $0.5/MMBtu and plant sized ranging from 2,500 to 10,000 tpd. The CIP price includes shipping DME 12,000 km at a cost of $1.10/MMBtu.
- From the Western Australia, varies from $4.00-$5.00/MMBtu with gas at $1.00/MMBtu and plant sized ranging from 2,500 to 10,000 tpd. The CIP price includes shipping DME 7,000 km at a cost of $0.60/MMBtu.

Based on the historical fuel prices for Japan from 1996, DME would be priced lower than LPG and Diesel, and equivalent to LNG.

3.4. Other topics to be presented include:
- Discussion of the general technical, marketing and commercial aspects of using DME as a LPG substitute, as a fuel for power generation, and as a diesel alternative.

4. Key Messages

Gas conversion is rapidly becoming a major gas utilization tool offering a third alternative to bringing gas to the market place after the well established pipeline and LNG options. Among the large scale, potential gas conversion technologies, GTL-FT is by far the most popular technology simply because it converts gas into conventional (though cleaner), easy to market liquid fuels such as diesel and naphtha, and also lubestocks. This paper shows that other gas conversion products such as oxygenates have great potential as advanced clean fuels and chemical feedstocks for the 21st century. Methanol is the enabling product in a “Natural Gas Park” both as a potential large volume fuel and as feedstock for numerous other fuels and chemicals. DME is the most promising methanol derivative, due to its potential as a clean, multi-purpose fuel and chemical feedstock. Methanol and DME as feedstocks for olefins could change the face of the chemical industry. Extensive on-going activities around the world are addressing the significant challenges that have to be overcome for the successful commercialization of oxygenates in the new markets. Significant global collaboration efforts are providing a foundation for creating a new global oxygenate business.

REFERENCES